ENVIRONMENTAL ASPECTS OF SEWAGE EFFLUENT DISINFECTION

—A REVIEW—

Ministry of the Environment

Ontario

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ENVIRONMENTAL ASPECTS

OF

SEWAGE EFFLUENT DISINFECTION

- A REVIEW -

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PREFACE

This is the first in a series of technical reports compiled by personnel of the M.O.E. Chlorination Committee. The findings will be used by the Committee as a basis for the development of a proposed M.O.E. policy statement dealing with chlorination and disinfection to be submitted to senior management for approval.

Thus, at present, the contents of this report do not constitute official Ministry of the Environment policy.

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INTRODUCTION

Chlorine in the form of chlorinated lime was first used in 1854 by the Royal Sewage Commission of London to deodourize sewage. It was not until 1887 that chlorine was used in the United States to deodourize and disinfect sewage. In 1909 liquid chlorine was produced and by 1914 was in use for the disinfection of sewage effluents.

Since that time, chlorination has become an essential component in the sewage treatment process. The present MOE practice is to require a minimum chlorine residual of 0.5 mg/l after a 30 minute contact time.

The primary objective of using chlorine for disinfection in wastewater treatment is the destruction of pathogenic microorganisms before discharge of wastewater to a receiver in order to safeguard public health. As such, the application of chlorine for the irradication of these pathogens has represented a significant advancement in the prevention of outbreaks of waterborne diseases. Some of these diseases which are capable of transmission by water are listed below:

- Typhoid Fever
- Cholera
- Amoebic Dysentery
- Gastroenteritis
- Schistosomiasis
- Paralytic Poliomyelitis
- Aseptic meningitis
- Respiratory diseases
- Enteritis
- Infectious Hepatitis
- Worms-Roundworms, Hookworms

Despite the wide-spread use of chlorine there have been some instances of outbreaks of water-borne diseases. Kornder (1974) reported an outbreak of typhoid fever in 1935 in Cochrane, Ontario associated with an unchlorinated surface water supply which also received the city's wastewater. In the early 1940's, Saskatchewan suffered many cases of typhoid related to an unchlorinated source of river water in a small northwestern city. Vancouver, British Columbia had an outbreak of typhoid in 1953 which was traced to an unchlorinated

effluent draining into a creek frequented by children. Also, in the same year, Vancouver had many cases of poliomyelitis which were traced back to a common swimming pool contact. In British Columbia in the late 1960's, many cases of typhoid occurred in a resort area and spread throughout the northwest part of the United States and to many parts of Canada. Of more recent vintage, was an outbreak of typhoid near Kingston, Ontario in 1975.

Despite the efficiency of chlorine as a germicide, many investigators have expressed concern regarding the environmental effects of chlorination practices on the aquatic ecosystem.

OBJECTIVES

In addition to its use in the disinfection of treated sewage effluent, chlorine is utilized in Ontario for a variety of purposes including disinfection of drinking water, the production of pulp and paper and for antifouling of cooling systems. However, the primary objective of this paper is to summarize the current information on the environmental and health aspects of disinfection with chlorine and to relate this to areas of concern associated with conventional disinfection practices in Ontario.

CHLORINE FUNDAMENTALS

Chambers (1971) gives a good account of the basic chemistry of chlorine.

Chlorine is usually applied to wastewater effluents as liquid chlorine (Cl_2), sodium hypochlorite (NaOCl), or calcium hypochlorite ($Ca(OCl)_2$). When chlorine is dissolved in water the following reaction occurs:

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^-$$

The HOCl (hypochlorous acid) ionizes in waters as follows:

$$HOCl \rightleftharpoons H^+ + OCl^-$$

As pH is increased, increasing amounts of HOCl are converted to hypochlorite ion (OCl^-). As pH is decreased the percentage of HOCl increases and that of OCl^- ion decreases. At normal operating pH levels, the hydrolysis of chlorine is essentially complete.

Hypochlorous acid (HOCl) is an extremely potent germicide and because it is a highly active oxidizing agent is short-lived in most wastewater effluents. Hypochlorous acid reacts with ammonia to form chloramines according to the following reactions:

$NH_3 + HOCl \rightarrow NH_2Cl$ (monochloramine) $+ H_2O$

$NH_2Cl + HOCl \rightarrow NHCl_2$ (dichloramine) $+ H_2O$

$NHCl_2 + HOCl \rightarrow NCl_3$ (nitrogen trichloride) $+ H_2O$

In addition to combining with ammonia, hypochlorous acid reacts with amino acids, proteinaceous materials, and organic matter to produce chlorine compounds that have low disinfecting power. It combines with sulfites, sulfides, nitrites and ferrous or manganous ions to produce compounds that have no germicidal activity.

All the interferences that germicidally remove effective chlorine from solution are referred to collectively as "chlorine demand" which may be defined as the difference between the amount of chlorine applied and the amount remaining at the end of the contact period. Servizi (1974) stated that chlorine combines with a wide variety of inorganic and organic materials, particularly reducing agents, and that these demands for chlorine must be satisfied before chlorine becomes available for disinfection. He further stated that chlorine, hypochlorous acid and hypochlorite ion are referred to as free available chlorine residuals while chloramines are termed combined available chlorine residuals and that since free and combined chlorine residuals have disinfecting powers, their sum is termed the total available chlorine residual.

Combined available chlorine is a much less efficient colicidal agent than free available chlorine (Fair and Gyer 1954).

Chlorine has been used to disinfect wastewater almost to the exclusion of all other germicidal agents largely because of its effectiveness in reducing the coliform count to acceptable levels much more economically than any other disinfectant. It would be axiomatic to state that some form of disinfection is necessary considering that public health is of paramount importance: however, paradoxically enough recent investigations into the toxic and carcinogenic effects of the total residual chlorine by-products of chlorination in wastewaters have indicated that problem areas may exist from the point of view of both public health and the environment.

POTENTIAL CARCINOGENIC EFFECTS OF TOTAL RESIDUAL CHLORINE

As yet there is a lack of information dealing with the possible carcinogenic effects of total residual chlorine components. The studies that have been done, however, have indicated that the possibility exists that carcinogenic effects could be related to the presence of chlorine-containing stable organics.

Jolley (1973) determined that under experimental conditions approximating those encountered in wastewater treatment plants, chlorine-containing organic compounds are present after chlorination of the effluent. Some seventeen chlorine-containing stable organic compounds were identified and quantified at the 0.2 to 4.3 ug/l level. A list of these chlorination products and their concentrations is given in Table 1. Under EPA contract, Ajami (1974) reviewed the literature for health hazards associated with these compounds or classes of compounds. Compounds listed in Table 1 fall under the general classification of (1) chlorophenols (2) chlorobenzoic and chlorophenylacetic acids and (3) chlorinated purines and pyrimidines. It was concluded that although the first two classes of compounds should not represent significant health hazards at those concentrations, the chlorinated purines and pyrimidines could potentially exhibit some teratogenic and carcinogenic activities.

Bellar et al (1974) determined the nature and concentrations of organochlorine compounds in the effluent of a wastewater treatment plant receiving a mixture of domestic sewage and industrial wastes. Based on the results presented in Table 2, Bellar et al concluded that the increase in chloroform concentration appeared to be due to chlorination. Similar conclusions could not be reached for the other compounds listed because of small differences in the concentration levels before and after chlorination.

Slightly tangential but nevertheless relevant are the findings of investigators concerned with the presence of chloroform and related compounds in drinking water supplies and their relation to potential carcinogenicity.

During the chlorine disinfection of municipal water supplies, Bellar et al (1974) found chloroform, bromodichloromethane and dibromochloromethane and assumed that these compounds were formed through the interaction of chlorine with organic compounds in drinking water. Table 3 lists the concentrations found at different sampling points at a water treatment plant.

TABLE 1: Tentative Identification and Concentrations of Chlorine Containing Constituents in Chlorinated Effluents

Identification	Concentration of Organic Compound (ug/liter)
5-Chlorouracil	4.3
5-Chlorouridine	1.7
8-Chlorocaffeine	1.7
6-Chloroguanine	0.9
8-Chloroxanthine	1.5
2-Chlorobenzoic acid	0.26
5-Chlorosalicylic acid	0.24
4-Chloromandelic acid	1.1
2-Chlorophenol	1.7
4-Chlorophenylacetic acid	0.38
4-Chlorobenzoic acid	1.1
4-Chlorophenol	0.69
3-Chlorobenzoic acid	0.62
3-Chlorophenol	0.51
4-Chlororesorcinol	1.2
3-Chloro-4-hydroxy-benzoic acid	1.3
4-Chloro-3-methyl-phenol	1.5

TABLE 2: Organochlorine Compounds in Water from Sewage Treatment Plants

Compound	Influent before Treatment	Concentration (ug/l) Effluent before Chlorination	Effluent after Chlorination
Methylene chloride	8.2	2.9	3.4
Chloroform	9.3	7.1	12.1
1,1,1-Trichloroethane	16.5	9.0	8.5
1.1,2-Trichloroethylene	40.4	8.6	9.8
1,1,2,2 - Tetrachloroethylene	6.2	3.9	4.2
Dichlorobenzenes	10.6	5.6	6.3
Trichlorobenzenes	66.9	56.7	56.9

TABLE 3: Trihalogenated Methane Content of Water from Water Treatment Plant

Sample Source	Sampling Point	Free Chlorine ppm	Concentration (ug/l) Chloro-form	Bromo dichloro-methane	Dibromo-chloro-methane
Raw river water	1	0.0	0.9	a	a
River water treated with chlorine and alum-chlorine contact time $\approx$ 80 min.	2	6.0	22.1	6.3	0.7
3-day-old settled water	3	2.0	60.8	18.0	1.1
Water flowing from settled areas to filters[b]	4	2.2	127	21.9	2.4
Filter effluent	5	Unknown	83.9	18.0	1.7
Finished water	6	1.75	94.0	20.8	2.0

[a]None detected. If present, the concentration is 0.1 ug/l.

[b]Carbon slurry added at this point.

Rook (1974) found the following compounds to be formed by chlorination of water supplies: chloroform, bromodichlormethane, dibromochloromethane and bromoform. He further postulated that naturally occurring humic substances were precursors to the formation of these haloforms. The maximum concentrations found were: chloroform 554 ug/l, bromodichloromethane 20.0 ug/l, dibromochloromethane 13.3 ug/l and bromoform 10.0 ug/l.

Kraybill (1974) in evaluating the health effects of some of these compounds indicated that both bromoform and chlorodibromomethane, which were presumably formed during disinfection with chlorine, were classified as "suspect carcinogens".

The Environmental Protection Agency Task Force Report on the Disinfection of Wastewater (1975) concluded that disinfection of water and wastewater with chlorine can result in the formation of halogenated organic compounds that are potentially toxic to man.

TOXICITY OF TOTAL RESIDUAL CHLORINE TO AQUATIC LIFE

As opposed to the relatively sparse amount of data dealing with the potential carcinogenic effects of halogenated organic compounds there is a considerable amount of information delineating the toxic effects of total residual chlorine to aquatic life.

Toxicity

Addition of chlorine to water containing sewage produces several species of chlorine compounds such as hypochlorous acid ($HOCl$), hypochlorite ion (OCl^-), monochloramine (NH_2Cl), dichloramine ($NHCl_2$) and trichloramine (NCl_3).

Merkens (1958) indicated that the toxicity of chlorine depends not on the amount of chlorine added but on the concentration of residual chlorine remaining in the solution and this in turn depends on the relative proportions of free chlorine ($HOCl$ and OCl^-) and chloramines of which it is composed. He also indicated that toxicities of chlorine and chloramine to fish are of the same order, with free chlorine being the most toxic. Rosenburger (1971) also found that free chlorine is the most toxic form of chlorine and that dichloramine appears to be more toxic than monochloramine to coho salmon.

Brungs (1973) concluded from the literature that the lethal effects of free chlorine to aquatic life are more rapid and occur at lower concentrations than those of chloramine, and indicated that environmental variables do not appear to effect residual chlorine toxicity significantly.

Modes of Chlorine Intoxification

Doudoroff (1957), Mann (1950), Penzes (1971), Pike (1971) and Dandy (1967, 1972)* attribute death of fish exposed to chlorine and its related compounds to damage to the epithelial cells of gills resulting in ultimate suffocation of the fish. In contrast, Forbes (1971), found that white sucker in one mg/l chlorine solution appeared nervous, more active, prone to darting and occasionally swam upside down. Their rapid operculating became irregular near death, and they gulped air at the surface. Some test fish displayed small points of hemorrhage in the caudal and anal region. Forbes hypothesized that chlorine enters through the gills and somehow, either directly or indirectly, affects the nervous system.

Eaton et al (1973) found that when they exposed the fathead minnow to water containing 1.5 ppm chloramine for about 40 minutes that metahaemoglobin was 32 percent (average) in the test fish, whereas the control fish had less than three percent. They concluded that chloramines may cause marked metahemoglobenemia in fish.

Dandy (1967, 1972)* showed that exposure of brook trout to chlorine evoked changes in activity, ventilation, the coughing reflex and, at lethal levels, a heavy secretion of mucus. Locomotory activity increased initially and was subsequently depressed. Both responses were seen at 0.35 and 0.08 ppm, but at the sublethal level of 0.005 mg/l, the initial increase in activity was not seen.

Zillich (1972) asked why, if chlorine is toxic to fish at very low levels, there are no fish kills below treatment plant outfalls. The answer is that fish are known to avoid toxic materials at concentrations well below those required to cause toxic symptoms. Sprague and Drury (1969) studied the avoidance response of rainbow trout and Atlantic salmon to chlorine. The fish can avoid the concentration of 0.01 mg/l which is lethal in 12 days, and of 1.0 mg/l which is rapidly lethal. However, the fish preferred 0.1 mg/l. It is uncertain that preference of rainbow trout for intermediate lethal chlorine levels resulted from a depressant effect on activity. The author observed that at the boundary with freshwater, the fish stopped short and turned back into chlorine. The momentary entrance into clean water apparently triggered an unpleasant sensation. Fava and Tsai (1973) found through experiments that the blacknose dace cannot discriminate and avoid sewage treatment plant effluents which are unchlorinated, or chlorinated to the level equivalent to chlorine demands of the effluents. The fish can discriminate and avoid chlorinated sewage effluents containing total residual chlorine as low as 0.01 mg/l.

*Canadian Studies

Hiatt et al (1953) found that a chlorine concentration of 10 mg/l produced violent irritation on fish, whereas 1.0 mg/l produced only slight irritation. They concluded that nearly all chemical irritants attack the common chemical senses.

Tsai (1975), Brungs (1973) and Servizi (1974)* offer comprehensive documentation of the toxicity of total residual chlorine to aquatic organisms. For the purposes of simplication the results and conclusions will be presented in two main categories (1) toxicity studies and (2) field studies.

Toxicity Studies

Brungs (1973) stated that many of the early toxicity investigations were of questionable value because no measurements were made of residual chlorine which declined at rates dependent upon the chlorine demand of the experimental water. Therefore, he recommended that continuous flow bioassay procedures be used for tests of residual chlorine toxicity.

Brungs cited many studies demonstrating total residual chlorine toxicity.

A residual chlorine concentration of 0.006 mg/l was lethal to trout fry in two days (Coventry et al, 1935) and the 7-day TL_{50} for rainbow trout was 0.08 mg/l with an estimated median period of survival of one year at 0.004 mg/l (Merkens, 1958). Sprague and Drury (1969) observed that rainbow trout were killed at 0.01 mg/l in 12 days and they avoided a concentration of 0.001 mg/l. Dandy (1969, 1972)* noted that Brook trout had a mean survival time of nine hours at 0.35 mg/l, 18 hours at 0.08 mg/l and 48 hours at 0.04 mg/l. Mortality was 67 percent after four days at 0.01 mg/l. Pike (1971) noted a fifty percent kill of brown trout at 0.02 mg/l within 10.5 hours and at 0.01 mg/l within 43.5 hours.

Arthur (1971-72) determined 96-hour TL_{50} values for the walleye, black bullhead, white sucker, yellow perch, large-mouth bass and fathead minnow. The observed concentration range was 0.09 to 0.30 mg/l. Coventry et al (1935) stated that 0.40 mg/l was fatal to sunfish and bullheads. Esvelt et al (1971) observed that the mean 96-hour TL_{50} value for golden shiners was 0.19 mg/l. Arthur and Eaton (1971) determined the safe concentration of residual chlorine for the fathead minnow to be 0.0165 mg/l in a chlorinated municipal water supply diluted with untreated water from Lake Superior. The 96-hour TL_{50} values for the fathead

*Canadian Studies

minnow were between 0.05 and 0.16 mg/l in diluted domestic wastewater treatment plant effluent (Arthur, 1972) (Zillich, 1969) and there was total mortality in clean, chlorinated water in three days at 0.154 mg/l (Arthur and Eaton, 1971).

Zillich (1972) used continuous flow, 4-day bioassays of effluent from two municipal sewage treatment plants on the fathead minnow, Pimephales promelas to assess toxic effects. Effluents from both plants were chlorinated following secondary treatment. The highest concentration of treated effluent from Plant 1 (which included metal plating wastes) at which survival was 100 percent in four days was 1.66 percent on a volume of effluent to water basis (V/V) and the lowest concentration causing abnormal behaviour was 1.25 percent V/V at which the mean residual chlorine was 0.04 mg/l measured amperometrically. Effluent from Plant 2 was slightly less toxic than from Plant 1, with the highest concentration of treated effluent at which survival was 100 percent in four days being 3.2 percent V/V. Sublethal stress was evident among fish held at 1.92 percent V/V at which the mean chlorine residual was 0.05 mg/l.

It is evident that the results of continuous flow bioassays indicate that low concentrations of total residual chlorine are either lethal or sublethal to a range of fish species. It is interesting to note that even when fish are exposed only briefly to chlorine concentrations, their capabilties of recovery when transferred to freshwater are somewhat minimal. Dandy (1972) determined that when brook trout were transferred directly into freshwater at the first signs of disequilibrium caused by chlorine, death always ensued even though life expectancy at the time of transfer from weaker lethal solutions was several hours. Pike (1971) observed essentially the same responses after transfer of affected brown trout to clean water. Brungs (1973) gives a good summary of the results of brief exposures of fish to residual chlorine (Table 4).

Field Studies

Tsai (1975) compiled field studies dealing with downstream toxic effects of chlorinated wastewater.

Hubault (1955, 1957) held roach in running water obtained from the river Muerthe and found that one of the toxic compounds in the water was chlorine. Tsai (1968, 1970) studied the effects of the chlorinated sewage treatment plant effluents on fish in the Patuxent River, Maryland. He found that chlorinated sewage effluents act first as toxic

TABLE 4: Summary of Results of Brief Exposure of Fish to Residual Chlorine

Species	Effect Endpoint	Time	Measured Residual Chlorine Concentration (mg/l)
Chinook Salmon	First death	2.2 hr	0.25
Brook Trout	Median mortality	80 min	0.5
Brook Trout	Mean survival time	9 hr	0.35
Brook Trout	Mean survival time	18 hr	0.08
Brook Trout	Mean survival time	48 hr	0.04
Brook Trout	Depressed activity	24 hr	0.005
Brown Trout	Total mortality	2 min	0.04
Rainbow Trout	Slight Avoidance	10 min	0.001
Rainbow Trout	Lethal	2 hr	0.3
Fingerling Rainbow Trout	Lethal	4-5 hr	0.25
Trout fry	Lethal	Instantly	0.3
Yellow Perch	TL_{50}	1 hr	>0.88
Yellow Perch	TL_{50}	12 hr	0.494
Smallmouth Bass	Median mortality	15 hr	0.5
White sucker	Lethal	30-60 min	1.0
Largemouth Bass	TL_{50}	1 hr	>0.74
Largemouth Bass	TL_{50}	12 hr	0.365
Fathead Minnow	TL_{50}	1 hr	>0.79
Fathead Minnow	TL_{50}	12 hr	0.26
Miscellaneous	Initial Kill	15 min	0.28
Miscellaneous	Erratic swimming	6 min	0.09

*TL_{50} = median tolerance limit (50 percent survival)

materials, which seriously reduce fish species diversity and abundance immediately below the effluent outfalls. Further downstream, where toxicity of chlorinated effluents decrease to such a degree that it is no longer harmful to fish life, then a species shift will result, probably due to organic enrichment and deoxygenation.

Wuerthele (1970a,b,c,d) held fathead minnows in live boxes in the Grand River and the St. Joseph River above and below the outfalls of the Lansing and Hillsdale sewage treatment plants in Michigan, at a distance of one and half and four and a half miles. The last cage at four and a half miles had 25 percent mortality. In continuous -flow bioassay using the same stream water and the effluent for 24 hours, the author found that no fish survived in wastewater with concentrations stronger than 25 percent and fish in concentration as low as 8.35 percent were unable to maintain themselves in the water column and probably would not have survived at this concentration during a longer bioassay or under river conditions.

Basch et al (1971) also held rainbow trout and fathead minnows for 96 hours in live boxes in the receiving streams above and below four different Michigan wastewater treatment plants. Fish held below these outfalls were subjected to both chlorinated and non-chlorinated exposures during effluent discharges. They found that residual chlorine was the principal toxic constituent of the chlorinated effluents which were toxic to rainbow trout at distances of up to 0.8 miles and to fathead minnows to 0.6 miles. The 96 hour TL_m of total residual chlorine for rainbow trout was 0.023 mg/l.

Zillich (1972) made on-site continuous flow bioassays at two Michigan wastewater treatment plants using chlorinated and dechlorinated sewage effluents. He showed that combined residual chlorine is the principal toxicant in these effluents. They were toxic to fathead minnows after they were diluted to two to four percent. The 96 hour TL_m for the fathead minnow was between 0.05 and 0.16 mg/l and 0.04 to 0.05 mg/l were considered as threshold concentrations. Tsai (1973) made comparative studies of water quality and fish species diversity in stream locations immediately above and below the outfalls of 149 secondary sewage treatment plants in Virginia, Maryland, and Pennsylvania. Streams which received heavily chlorinated sewage often had clean bottoms, without living organisms in the area immediately below the outfall. These bottoms differed greatly from those in natural upstream conditions where algae and other vegetation were present. It also differed from the bottoms of streams receiving

unchlorinated sewage where sewage fungi usually grew in abundance. No fish were found in water with total chlorine of 0.37 mg/l and the species diversity index went to zero in 0.25 mg/l. The species diversity index was reduced 50 percent at 0.1 mg/l total chlorine and 25 percent at 0.025 mg/l. In this particular study plants in Maryland and Virginia maintained a total chlorine residual of 0.5 to 2.0 mg/l in the effluents with Pennsylvania requiring 0.5 mg/l in effluents prior to discharge to natural surface water.

Arthur (1972) studied the effect of chlorinated secondary wastewater treatment plant effluent containing only domestic waste on reproduction of fathead minnows, Daphnia magna and the scud Gammarus pseudolimnaeus. Daphnia magna died at a residual chlorine concentration of 0.014 mg/l and acceptable reproduction occurred at 0.003 mg/l and below. Scud reproduction was reduced at residual chlorine concentrations (amperometric titration method) above approximately 0.012 mg/l (1.2 percent effluent). No toxic effect was observed when the same waste was unchlorinated or dechlorinated (with sulphur dioxide) or disinfected with ozone at effluent concentrations as high as 10 percent.

Arthur also conducted acute toxicity studies with eight species of fish, crayfish (Orconectes rusticus), scud (Gammarus pseudolimneaus), snails (Physa integra) and Campeloma decisum) and stoneflies (Acroneuria lycorias). His studies indicated that the crayfish and snails were least sensitive (7-day TL_{50} values greater than 0.78 mg/l). Seven-day TL_{50} values for the other organisms were between 0.083 and 0.261 mg/l residual chlorine, Coho salmon and brook trout were the most sensitive. Nearly 50 percent of these observed mortalities occurred in the first 12 hours of the acute tests, indicating that the lethal effect of residual chlorine occurs rapidly but not as rapidly as if free chlorine were present.

Esvelt et al (1971, 1973) and Krock and Mason (1971) conducted an extensive study on the toxicity of chlorinated municipal wastewaters entering San Francisco Bay and surrounding areas. They observed a significant increase in toxicity following chlorination. Chlorine toxicity was still significant in aged (up to three days) chlorinated wastewater, in which residual chlorine concentrations were as high as 25 percent of the initial level. Rainbow trout was the most sensitive of the species tested, followed by the golden shiner and three-spined stickleback. A calculated chlorine residual of 0.03 mg/l based on dilution of a measured concentration

of 2.0 mg/l reduced plankton photosynthesis by more than 20 percent of the value obtained with a dilution of effluent having no chlorine residual. One of the conclusions of this study was that chlorination may be the largest single source of toxicity in San Franciso Bay.

Martens and Servizi (1974) and Servizi and Martens (1974) observed mortality of salmon in receiving streams of TRC concentrations as low as 0.02 mg/l. Lethal concentrations persisted in undiluted effluent for at least 50 hours. Twenty to one dilutions resulted in the chlorine residual declining to a non-detectable concentration after 12 hours. Studies with live cages at points downstream from the effluent demonstrated acutely lethal conditions that did not persist during periods when the chlorinator was inoperable.

The Ontario Ministry of the Environment in assessing the impact of the Milton sewage treatment plant on Oakville Creek water quality stated that chlorination resulted in a residual concentration entering the stream with this residual becoming a damaging factor. Biological work revealed that the benthic macroinvertebrate community extending from the sewage treatment plant one or two miles downstream was considerably impaired. The investigators concluded that since the greatest benthic invertebrate impairment was just downstream from the sewage plant effluent, rather than further downstream where the lowest dissolved oxygen readings were found, the toxic components of the effluent (e.g. chlorine) had a greater effect on the invertebrate population than the dissolved oxygen depletion resulting from the organic and nutrient loadings. Veal (personal communication) related the details of a fish kill associated with the Milton sewage treatment plant in June 1973. A fish kill investigation was conducted in relation to a strong chlorine odour downstream from the sewage treatment plant. At selected stations downstream from the plant outfall dead fish were observed. The dead fish included shiners, suckers, chub and dace. It was roughly estimated that perhaps 100 to 200 fish died. Samples for free residual chlorine were taken immediately below the sewage outfall and another taken further downstream. The sample taken directly below the outfall contained 5.0 mg/l chlorine while the other station had 0.75 mg/l chlorine. It was therefore concluded that the fish kill was caused by a high concentration of chlorine accidentally entering Oakville Creek as a result of problems in switching from one chlorine contact chamber to another in the sewage treatment plant.

In assessing the water quality of German Mills Creek in relation to the Pugsley Street sewage treatment plant, Ontario Ministry of the Environment investigators concluded that for a distance of approximately two miles downstream of

the plant outfall, levels of residual chlorine and ammonia indicated toxic conditions for most stream biota. Residual chlorine levels up to 1.9 mg/l were measured in the final plant effluent.

Veal (personal communication) related that benthic macroinvertebrate sampling in the vicinity of the Humber sewage treatment plant effluent in Lake Ontario revealed that a zone approximately 1000 feet in diameter at the outfall was completely void of organisms and contained leaf litter which did not appear to be decomposing. Upon investigation, it was found that chlorine residuals in the final plant effluent were not being measured on a routine basis. The study indicated that the lack of quality control probably resulted in the discharge of total residual chlorine levels higher than the Ministry objective of 0.5 mg/l after a 30 minute contact time.

CITED RECOMMENDATIONS-SAFE LEVELS OF TOTAL RESIDUAL CHLORINE

Brungs (1973) in reviewing the literature on the toxicity of residual chlorine produced the following guidelines:

Type of Chlorination	Residual Chlorine	Concentration of Total Degree of Protection
Continuous	A. Not to exceed 0.01 mg/l	This concentration would not protect trout and salmon and some important fish food organisms, it could be partially lethal to sensitive life stages of sensitive fish species.
	B. Not to exceed 0.002 mg/l	This concentration should protect most aquatic organisms
Intermittent	A. For a period of 2 hours a day up to, but not to exceed 0.2 mg/l	This concentration would not protect trout and salmon
	B. For a period of 2 hours a day, up to but not to exceed 0.04 mg/l	This concentration should protect most species of fish
	C. For a period of ½ hour a day, up to but not to exceed 0.01 mg/l	This concentration should protect trout and salmon if high concentrations of free chlorine persist.

In conclusion, Brungs recommended a criterion for safe levels of 0.01 mg/l for warmwater fish and 0.002 mg/l for coldwater species and the most sensitive fish food organisms. Basch and Truchan (1974) recommended maximum concentrations of 0.02 and 0.005 mg/l for warmwater and coldwater fish, respectively. The U.S. Environmental Protection Agency in its publication "Water Quality Criteria, 1972" recommended a guideline to protect all aquatic life in receiving streams. For continuous exposure, a level of 0.003 mg/l chlorine must not be exceeded anywhere in the receiving stream. For intermittent discharges, the recommended level of 0.05 mg/l total residual chlorine for a period of 30 minutes in any 24 hour interval is less restrictive than Brung's recommendations of 0.01 mg/l total residual chlorine for 30 minutes in 24 hours. As opposed to the aforementioned, Tsai (1973) indicated that if all species of fish were to be protected in areas immediately below sewage outfalls, the standard would be no detectable total residual chlorine in water.

AREAS OF CONCERN

A comparison of the recommendations of Brungs, Basch and Truchan and the U.S. Environmental Protection Agency with accepted chlorination practices at sewage treatment plants in Ontario yields certain areas of concern from an environmental point of view.

With regard to chlorination practices in sewage treatment plants in relation to in-stream environmental impact, three factors are important. These are:

1. total residual chlorine levels in sewage discharge;
2. the use of the orthotolidine method in measuring the aforementioned levels, and
3. the relationship between streamflows and STP discharges involving physical and chemical factors for both (mixing zones).

Total Residual Chlorine Levels

Notwithstanding problems associated with contact chamber retention time and proper mixing in the contact chamber, the conventional practice to ensure that the chlorine demand of the sewage had been met is to maintain a 0.5 mg/l chlorine residual in the chlorinated effluent.

Aside from arguments concerning the efficiency of chlorination as a bacteriocide and viricide, the fact remains that total chlorine residual of 0.5 mg/l is far in excess of the recommended safe concentrations for most aquatic organisms (0.002 mg/l measured as total residual chlorine).

Analytical Techniques

Servizi (1974) in recognizing that it is common practice to measure chlorine residuals in sewage using the colour comparator orthotolidine method stated that this method consistently gives lower values when applied to sewage or polluted waters than the indirect (back-titration) iodometric method employing either the starch-iodide or amperometric end points. The magnitude of the difference is not constant and can be on the order of 2 to 5 mg/l and in many sewage and waste mixtures even greater differences may be found (Standard Methods, 1971). Sawyer (1957) measured chlorine residuals in sewage using amperometric and orthotolidine methods and reported that the former measured up to 9.5 times as much as the latter.

Monroe and Phillips (1972) reported that the orthotolidine method failed to detect chlorine in treated sewage when the iodometric method measured about 1 mg/l chlorine or less. Servizi and Martens (1974) reported amperometric measurements of chlorine residuals in treated sewage averaged about 8 times those obtained with the orthotolidine colour comparator method. They recommended that the amperometric method of measuring chlorine residual be adopted. Similarly, Collins and Deaner (1973) recommended the amperometric method be adopted in place of the orthotolidine or the modified iodometic method. In a survey of 36 sewage treatment plants in California, White (1974) observed that nine used the orthotolidine method to measure chlorine residuals and coincidently used excessive amounts of chlorine. In summation, Servizi (1974) concluded that in the interest of accuracy and fish protection, the amperometric method of measuring chlorine residual is recommended.

In comparing the recommendations of Brungs (1973) and the U.S. Environmental Protection Agency (1973) with the concept of maintaining a 0.5 mg/l total residual chlorine level in sewage treatment plant effluent coupled with the relatively insensitive orthotolidine analytical technique employed to monitor the aforementioned level, it became apparent that in all probability one could anticipate lethal or sub-lethal effects on downstream biota as a result.

Mixing Zone Concept

The magnitude of the environmental effect of lethal concentrations of total residual chlorine depends upon the conformation and behaviour of the mixing zone in relation to morphological, chemical and physical characteristics of the stream as well as the mode of effluent discharge.

At this juncture it is important to consider what is meant by the term "mixing zone" in relation to the problem at hand. A mixing zone can be defined as "an area contiguous to a point source, where exceptions to water quality objectives and conditions otherwise applicable to the receiving water body may be granted" (Great Lakes Water Quality Board-IJC, Water Quality Objectives Subcommittee Report, Appendix A, 1974). In conjunction with this definition Leggatt (personal communication) outlined guidelines of general biological consideration based on a synthesis of information taken from the Guidelines and Criteria for Water Quality Management in Ontario, Environmental Protection Agency, Water Quality Criteria, 1972, and Great Lakes Water Quality Board-IJC, Water Quality Objectives Subcommittee Report, Appendix A, 1974.

1. No situation should exist within a mixing zone which can cause:

    a. rapid lethal effects to important aquatic life;
    b. irreversible responses resulting in detrimental post-exposure effects; or
    c. bioconcentration of toxic materials which may be harmful to the organism or its consumer.

2. Rapid changes in water quality cause stress to the aquatic communities through shock effect and hence should be avoided.

3. Concentration of toxic materials at any point in the mixing zone where important species are physically capable of residing should not exceed an appropriate LC 50. The mixing zone should be considered as a region in which organism response to water quality characteristics is time-dependent. In order to protect drifting and both weak and strong swimming organisms in a mixing zone, data should be developed to demonstrate that the organism can survive without irreversible damage. This time-exposure should be based on the maximum expected residence time, including consideration of attraction properties and avoidance stimulating properties of some toxic substances to certain aquatic species.

4. Mixing zones should not form a barrier to migrating routes of aquatic species. To prevent blocks to passage less than one third the stream width should be used as a mixing zone (MOE-zone of passage guidelines in "Guidelines and Criteria for Water Quality Management in Ontario").

With respect to condition 1, and with an assumed total residual chlorine concentration of 0.5 mg/l (although it is probably much higher) it would be anticipated that at least some portion of the mixing zone would be rapidly lethal to some aquatic organisms immediately below the outfall (Sprague and Drury, 1969, Dandy 1969, 1972, Pike, 1971). As noted above, Leggatt (personal communication) stated that there should be no irreversible responses resulting in detrimental post-exposure effects. Dandy (1972), Pike (1971) and Brungs (1973) indicated that even brief exposures to chlorinated wastewater resulted in death for the specific organisms tested.

With respect to condition 2, Brungs (1973) in summarizing acute and chronic toxic effects of total residual chlorine on aquatic life found that depending upon the species tested, total residual chlorine concentrations ranging from 0.005 to 0.261 mg/l exerted effects ranging from depressed activity to 100 percent kill within a short period of time. The TL_{50} test was the method used most often.

Condition 3 stated that to prevent the blocks to passage for migrating routes of aquatic species no more than one-third of the stream width should be used as a mixing zone (Guidelines and Criteria for Water Quality Management in Ontario, MOE, 1974). The data presented in Table 5 (Choo-Ying to Ellis, February 6, 1976) represents stream flows and streamflow/sewage ratios at selected sewage treatment plants. These streamflow measurements are annual minimums averaged over seven consecutive days for three return periods, 1.575 years, 5 years, and 20 years.

These data yield some important information. Aside from the factor of stream width a comparison of the Uxbridge and Aurora sewage treatment plants, for example, indicates that there is a wide variability in the dilution potential of the receiving stream. Conceivably the dilution potential of the Uxbridge plant is greater than at the Aurora plant simply because the discharge of the Uxbridge plant constitutes a much smaller percentage of the total streamflow. By the same token, it is possible that depending upon the physical characteristics of the stream either or both plants could create a chemical barrier to upstream migration of aquatic organisms. Conversely, given sufficient stream width and proper plume formation, it is possible that neither situation would constitute a chemical barrier.

Assuming all else to be equal, all ratios of streamflow to sewage discharge flows indicate that in all probability, the stream water quality below these outfalls would exert some type of environmental stress on the aquatic fauna (Zillich

TABLE 5: Sewage Discharge from STP's and Minimum 7-Day Streamflows

STP	STP Discharge (cfs)		Streamflow above STP			Ratio: Max Sewage Discharge/Streamflow above STP		
	Mean Day	Max Day	7Q1.575	7Q5	7Q20	7Q1.575	7Q5	7Q20
Orangeville	2.0	3.0	4.3	2.1	0.6	1:1.43	1:0.70	1:0.20
Georgetown	3.5	5.0	7.8	4.2	1.7	1:1.56	1:0.84	1:0.34
Richmond Hill	3.5	5.6	0.0	0.0	0.0	------	------	------
Milton	2.2	2.7	6.7	1.3	0.0	1:2.48	1:0.48	------
Bolton	0.8	1.1	16.9	11.3	7.5	1:15.36	1:10.27	1:6.82
Uxbridge	0.5	1.0	9.0	7.6	6.4	1:9.00	1:7.60	1:6.40
Alliston	1.0	1.8	15.2	13.5	12.0	1:8.44	1:7.50	1:6.70
Markham	1.9	3.7	0.5	0.0	0.0	1:0.14	------	------
Aurora	2.6	5.6	0.0	0.0	0.0	------	------	------
Newmarket	3.6	13.0	0.0	0.0	0.0	------	------	------
Acton	1.1	1.3	2.1	1.0	0.2	1:1.62	1:0.76	1:0.15

1972, Wuerthele, 1970) for varying distances downstream. This stress could range from small behavioural aberrations to rapid lethal effects and is species dependent.

Concerning the avoidance reaction of aquatic organisms to chlorine, Sprague and Drury (1969) in studying the avoidance response of rainbow trout and Atlantic salmon to chlorine observed that concentrations of 0.01 mg/l (lethal in 12 days) and 1.0 mg/l (rapidly lethal) were avoided but that the fish "preferred" 0.1 mg/l to freshwater. Presumably at least somewhere in a mixing zone the total residual chlorine level will be 0.1 mg/l. It is possible that rainbow trout, for instance, could be attracted to this concentration of intermediate lethality within the mixing zone and as a result, suffer sizeable mortalities. The fact that rainbow trout avoid total residual chlorine concentrations of 0.01 and 1.0 mg/l poses problems if these concentrations are present in discharge water that for various reasons form a barrier across a stream or river in that it would effectively inhibit upstream migrations (Tsai, 1968, 1973). Likewise, mixing zones that contain chlorine concentrations that can be avoided by rainbow trout present yet another problem in that depending upon the size, shape and general conformation of the mixing zone, trout could be excluded from availing themselves of food sources and spawning grounds, etc. Concomitantly, the food sources for most species within the mixing zone would in all probability have been reduced to one extent or another as a result of high total chlorine residual content of the effluent. As a result, it would be anticipated that not only fish, but many benthic invertebrates as well would suffer general losses in populations and distributions. The resultant loss in recreational capability (i.e. fishing) of a particular watercourse could be quite extensive.

ALTERNATIVES TO CHLORINATION

It is not the intent of this paper to delve into the issue of alternatives to chlorination. However, it should be noted in passing that, because of concerns over possible health and environmental effects of chlorination, studies have been undertaken by several groups including the Ministry of the Environment into alternatives. These alternatives include ozonation, gamma irradiation, de-chlorination and the use of bromine chloride.

Also of pertinence to the chlorination issue are questions by some researchers both as to the actual efficiency of chlorination in the destruction of pathogenic micro-organisms and as to whether chlorination or in fact any disinfection of sewage effluent is indeed required in all circumstances.

PRESENT STUDIES

The Ontario Ministry of the Environment is presently engaged in studies dealing with the extent and magnitude of total residual chlorine levels in receiving streams downstream from three southern Ontario sewage treatment plants. Studies are also being conducted on laboratory and in situ total residual chlorine decay rates as well as methodologies for the measurement of total residual chlorine.

The results of these studies will be available in the near future.

CONCLUSIONS

1. Disinfection of water and wastewater with chlorine can result in the formation of halogenated organic compounds that are potentially toxic to man.

2. Disinfection of wastewater with chlorine can result in a residual chlorine level that is toxic to aquatic organisms including fish. The data indicate that chlorine concentrations in excess of 0.01 mg/l and 0.002 mg/l have an adverse effect on warm and cold water fish respectively.

3. It is suspected that in some cases the current practice of maintaining a total chlorine residual of 0.5 mg/l in STP effluents can have a detrimental effect on the aquatic environment. Furthermore, the orthotolidine analytical technique is an unreliable method of accurately measuring total residual chlorine concentrations.

4. There are very few definitive in-stream studies in Ontario concerning the impact of chlorinated effluent discharges from sewage treatment plants on the aquatic ecosystem.

RECOMMENDATIONS

1. Guidelines should be developed for case-by-case evaluations to ensure that both the public health and the aquatic environment are safeguarded with respect to future considerations for proposed sewage treatment plant installations as well as existing plants and proposed plant expansions.

2. With respect to the development of guidelines and policy statements on the subject of chlorination and disinfection the following issues should be considered:

   i the results of studies involving possible alternatives to chlorination such as ozonation, dechlorination, gamma irradiation, etc.

   ii the efficiency of the chlorination procedure in conventional sewage treatment plant operations.

   iii whether or not sewage effluent chlorination or disinfection of any kind is really required in certain circumstances.

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